# The Dependence of the Diffusion Parameters on the Dissolved H Concentration in the Dilute Phase of Pd−H

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## Introduction

With special reference to H diffusion in metals and alloys, diffusion constants, $D_H(c_H)$, determined from flux measurements, J, are a function of the H concentration, $c_H$, where $D_H(c_H)$ is defined by $J=-D_H(c_H)dc_H/dx$. The concentration-independent diffusion constant, $D_H^*$, appears in the following equation for the flux, $J=-D_H^*(c_H/RT)\ (d\mu_H/dx)$ where $\mu_H$ is the H chemical potential.

From these two expressions for J, $D_H^*$ can be obtained from $D_H$, i.e.,

$$D_H=D_H^*\ f(r) \qquad (1)$$

where f(*r*), the thermodynamic factor, is defined as

$$f(r)= (\partial\mu_H/RT/\partial \ln r)_T = (\partial \ln p^{½}/\partial \ln r)_T \qquad (2)$$

where p is the $H_2$ pressure in equilibrium with the H-containing metal phase and *r*=(H/metal), atom ratio, which is convenient to substitute for $c_H$ in most situations.

Determinations of $D_H^*$ from experimental $D_H$ values have been carried out for Pd-H and Pd-alloy-H systems by Wicke and his students [1]. They employed equation (1) under conditions where *r* is nearly constant, e.g., they employed a breakthrough method where an increment of H is added to one side of a membrane and the time for the disturbance to reach the other side can be used to calculate $D_H$. In such an experiment *r* is essentially constant permitting equation (1) to be employed at the given *r* value. The thermodynamic factor was determined as a function of *r* from isotherms for the Pd-H and Pd-alloy-H systems. Kűssner [2] determined $D_H$ for the $Pd_{0.77}Ag_{0.23}$ alloy over an H content range from *r*=0 to 0.42 (303 K) and Zűchner and Boes [3] carried out similar experiments at 296 K which included the $Pd_{0.60}Ag_{0.40}$ alloy. These alloys do not form hydride phases at these temperatures and therefore they were able to measure $D_H$ over a continuous range of *r* from which $D_H^*$ values were derived.

Salomons et al [4] measured diffusion constants for Pd from the relaxation time constants for weight changes of Pd samples resulting from sudden pressure changes. $D_H$ values were determined at 473, 513, 563 and 603 K as a function of *r* up to about 0.08. They found a decrease of $D_H(c_H)$ from *r*=0.015 to ≈0.08 and it was explained in terms of the thermodynamic factor times the so-called availability factor, (1−*r*), which allows for the blocking of interstices by H. They did not measure the dependence of $E_D$ on *r*.

In this paper the dependences of $D_H$, $D_H^o$ and $E_D$ on $r$ will be discussed from a general point-of-view where these parameters are defined by the Arrhenius equation for the diffusion constant, i.e.,

$$D_H = D_H^o \exp -(E_D/RT). \qquad (3)$$

## Results and Discussion

### Theoretical Considerations

The experimental dependences of $D_H$, $D_H^o$ and $E_D$ on $r$ will be considered from the viewpoint of a simple model of H in Pd and its alloys valid at small H contents. This is the lattice gas, mean field model given by

$$\mu_H = \mu_H^o + RT \ln [(1-r)/r] + \mu_H^E(r) \approx \mu_H^o + RT \ln [(1-r)/r] + g_1 r \qquad (4)$$

where $\mu_H$ is the chemical potential of the dissolved H and $\mu_H^o$ refers to conditions of $r \rightarrow 0$ without the ideal configurational term and $\mu_H^E(r)$ is the non-ideal or excess chemical potential which, at small $r$, can be approximated by $g_1 r$ where $g_1$ is a constant at a given temperature and it is the first order coefficient in a polynomial expansion of $\mu_H^E(r)$ in $r$ [5]. At equilibrium, $\mu_H$ in the metal phase must be equal to $\mu_H$ in the gas phase, $\frac{1}{2}\mu_{H2}^o + RT \ln p^{1/2}$, and therefore equation (4) can be rewritten as

$$\frac{1}{2}\mu_{H2}^o + RT \ln p^{1/2} = \mu_H = \mu_H^o + RT \ln [r/(1-r)] + g_1 r. \qquad (5)$$

Since $g_1$ is a partial free energy, it can be expressed in terms of the partial excess enthalpy and entropy, $g_1 = h_1 - Ts_1$. Values of these parameters for Pd−H have been given by Kuji et al [6] based on experimental data over the range 250-650 K; they are all negative for Pd−H. For example, at 373 K, $g_1 = -46.1$ kJ/ mol H, $h_1 = -82.5$ kJ/ mol H and $s_1 = -97.5$ J/K mol H [6]. The $g_1$ values are obtained from slopes of plots of $RT \ln p^{1/2}$ $[(1-r)/r]$ against $r$ and $h_1$ and $s_1$ can be derived from the slopes and intercepts of plots of $(g_1/T)$ against 1/T. The $g_1$ can be viewed as an H−H interaction free energy which leads to hydride formation below the critical temperature of 565 K [7].

From equations (1), (2) and (5) an expression for the thermodynamic factor, $f(r)$, can be obtained

$$f(r) = 1/(1-r) + g_1 r/RT. \qquad (6)$$

From equations (1) and (6), an expression for $\ln D_H$, appropriate for small $r$, can be derived

$$\ln D_H = \ln D_H^* + \ln f(r) = \ln D_H^* + \ln [(1/(1-r)) + g_1 r/RT] \approx \ln D_H^* + g_1 r/RT \qquad (7)$$

because at small $r$, $(1/(1-r))$ reduces to 1 and therefore $f(r)$ becomes $g_1 r/RT$.

If the derivative of $\ln D_H$ is taken with respect to 1/T in equation (7), we obtain

$$E_D - E_D^* = - h_1 r \qquad (8)$$

where $E_D^*$ indicates the concentration-independent $E_D$. From equation (3) and equations (7) and (8) , we obtain

$$\ln (D_H^o/D_H^{o,*}) = - s_1 r /R \qquad (9)$$

where $D_H^{o,*}$ is the concentration-independent $D_H^o$.

Thus, at small $r$, the changes of these excess thermodynamic functions with $r$ are given as

$$(d \ln D_H/dr) = g_1/RT;\ (d E_D/dr)/RT = - h_1/RT;\ (d \ln D_H^o/dr) = -s_1/R. \qquad (10)$$

It is of interest that experimental kinetic parameters, e.g., $(d \ln D_H/dr)$, can be equated to experimental thermodynamic parameters, e.g., $g_1/RT$.

## Experimental Results

The $r$ dependence of $D_H$ and $E_D$ were determined experimentally from H permeation through a Pd membrane. The downstream $p_{H2}$ was ≈0 while the upstream $p_{H2}$ was maintained at the desired values as determined from the $p_{H2}$-$r$ isotherms. For these boundary conditions [8] at relatively small H contents, it can be shown that, $(r_{up}/2) \approx r_{av}$ and the H/Pd values shown in Figure 1 are $r_{av}$ values.

An example of the changes of $\ln D_H$ and $E_D$ with $r$ for diffusion of H at 423 K in the dilute phase of Pd are shown in Figure 1 where it can be seen that the former decreases, while the latter increases, with $r$ as predicted. Their slopes give $g_1 = -37$ kJ/ mol H and $h_1 = -91.6$ kJ/ mol H which are reasonable for this temperature since a solubility isotherm at 423 K measured here gives $g_1 = -35.9$ kJ/mol H. The value of $h_1$ from isotherms is not as reliable as the value of $g_1$ and Kuji et al [5] give $h_1 = -82.5$ kJ/ mol H.
It can be concluded that $\ln D_H$ and $E_D$ change with $r$ in predicable ways for the dilute phase of Pd−H. These changes are significant at, e.g., 423 K, $E_D$ increases from about 23.9 ($r$=0) to 25.5 kJ/ mol H at $r$=0.02.

Oates and Mohri [9] have used the cluster variation method to describe the Pd—H system concluding that, in addition to the long range non-configurational interaction [10], there is a shorter range non-ideal configurational interaction of the H atoms which is, of course, accompanied by a non-ideal configurational entropy reflected by $s_1$. The increase of $E_D$ with $r$ suggests that the formation of the transition state causes some weakening of the H−H attractive interaction. The $s_1$ term is negative and therefore the non-ideal configuration of the H atoms is partially destroyed by diffusion leading to an increase of the partial excess entropy, $-s_1$.

A more complete account of the dependences of $D_H$ and $E_D$ will be given elsewhere [8]. The strict equating illustrated here of experimental kinetic parameters with thermodynamic parameters, $h_1$, $g_1$ and $s_1$, is noteworthy.

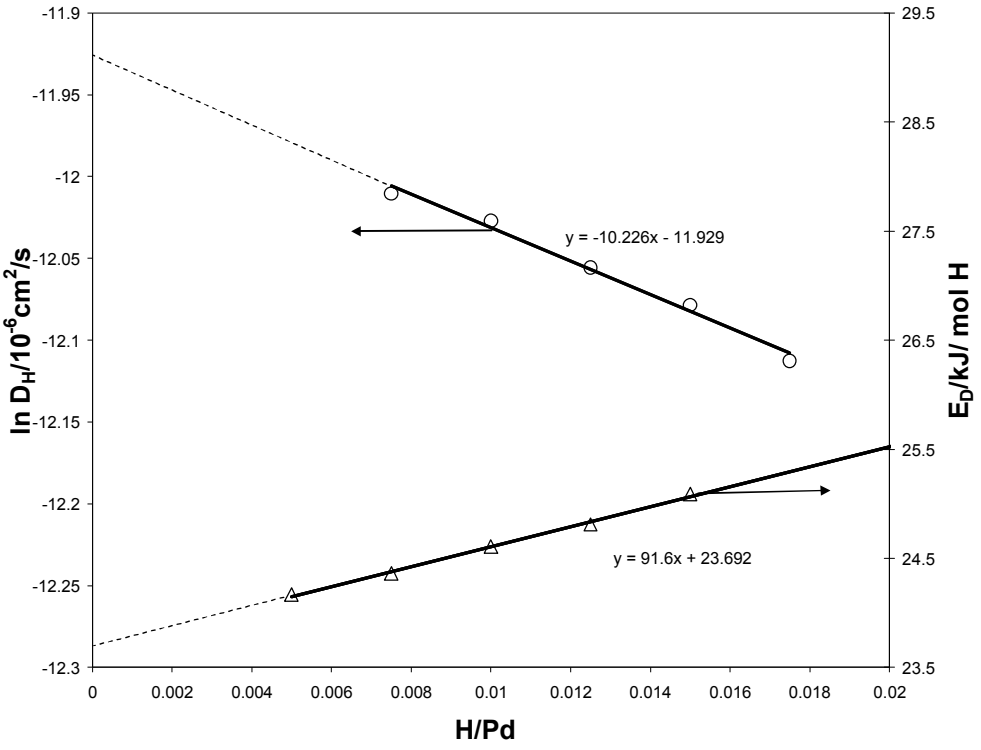


Figure 1. H Diffusion parameters for a Pd membrane (75 μm) at 423 K. o, ln $D_H$ Δ, $E_D$.

## References

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